# Linear absorption as a tool to measure the exciton delocalization length in molecular assemblies

Bakalis, Lisette D.; Knoester, Jasper

*Published in:*
Journal of Luminescence

*DOI:*
10.1016/S0022-2313(99)00231-8



*Publication date:*
2000

ELSEVIER

Journal of Luminescence 87–89 (2000) 66–70

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

Invited Paper

# Linear absorption as a tool to measure the exciton delocalization length in molecular assemblies

Lisette D. Bakalis, Jasper Knoester*

*Institute for Theoretical Physics and Materials Science Center, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

**Abstract**

Using numerical simulations, we study the possibility to determine the exciton delocalization length in molecular aggregates from the width of the linear absorption spectrum. We show that, in practice, the most useful approach is not based on the well-known exchange narrowing of the line width, but rather on the typical separation between the two lowest exciton states lying in one delocalization interval. We discuss the application to pseudo-isocyanine (PIC) *J* aggregates and the bacterial antenna complex LH2. 

*Keywords:* Molecular assemblies; Antenna systems; Delocalization length; Excitons

## 1. Introduction

The extent of the Frenkel exciton wave functions in molecular assemblies, determined by the competition between intermolecular transfer interactions and (static) disorder, has been a central issue over the past decade. In this context the B850 ring of the bacterial light harvesting complex LH2 has recently drawn particular attention. Claims concerning the extent of the excitons in this system range from a few (2–4) molecules to the entire ring (18 molecules) [1–6]. Various experimental techniques exist to obtain information on this length. Examples are the absorption linewidth (exchange narrowing) [7,8], the spontaneous emission rate (superradiance) [9], and the pump–probe spectrum (Pauli exclusion) [10,11]. As these different methods are not necessarily sensitive to the same properties of the exciton wave functions, they may differ in their results [4].

In this paper, we return to the absorption linewidth as a tool to measure the delocalization length. We argue that this width should not be used in the conventional way (exchange narrowing), but should rather be interpreted as the energy separation between the two lowest exciton states on one localization segment. Using numerical simulations, we compare the delocalization length obtained in this way to the "real" delocalization length obtained from the participation ratio of the exciton wave functions. Thus, we establish the validity and limitations of this approach.

The outline of this paper is as follows. In Section 2, we give the two different physical arguments that relate the absorption linewidth to the delocalization length. In Section 3 we present the results of our numerical simulations, while in Section 4 we discuss the implications of our results for pseudo-isocyanine (PIC) *J* aggregates and the LH2 antenna system. Finally, we conclude in Section 5.

## 2. Scaling arguments

We consider linear molecular aggregates consisting of *N* two-level molecules. The Frenkel exciton Hamiltonian for this model reads

$$\hat{H} = \sum_{n=1}^{N} (\omega_0 + \varepsilon_n)\hat{b}_n^{\dagger}\hat{b}_n + \sum_{n=1}^{N-1} J(\hat{b}_n^{\dagger}\hat{b}_{n+1} + \hat{b}_{n+1}^{\dagger}\hat{b}_n). \quad (1)$$

* Corresponding author. Tel.: +31-50-3634369; fax: +31-50-3634947.

*E-mail address:* knoester@chem.rug.nl (J. Knoester)

0022-2313/00/$ - see front matter 
PII: S0022-2313(99)00231-8

Here, $\hat{b}_n^\dagger$ and $\hat{b}_n$ denote the Pauli creation and annihilation operators, respectively, for an excitation on molecule $n$, $\omega_0$ is the average molecular transition energy, and $J$ is the nearest-neighbor excitation transfer interaction. Static disorder is incorporated through the offsets $\varepsilon_n$, which are independently chosen from a Gaussian distribution with standard deviation $\sigma$ (FWHM $2.35\sigma$). We use open boundary conditions and set $\hbar = 1$. We stress that the boundary conditions are not important, as we will mostly focus on the regime where the delocalization length is much smaller than the aggregate size.

The linear absorption spectrum of the model Eq. (1) has been studied extensively [12,13]. For $J$-aggregates ($J < 0$) and $\sigma$ at most of the order of $|J|$, the spectrum lies at the lower exciton band edge ($\omega \sim \omega_0 - 2|J|$). Its shape is asymmetric, with a Gaussian low-energy wing and a more pronounced high-energy wing. Concerning the width of the spectrum, two simple arguments can be made, which both start from the situation of an ordered aggregate ($\sigma = 0$). In this situation, the one-exciton states, which determine the absorption spectrum, are given by

$$|k\rangle = \sum_{n=1}^{N} \sin\left(\frac{\pi k n}{N+1}\right) \hat{b}_n^\dagger |0\rangle, \tag{2}$$

where $k = 1, 2, \ldots, N$ and $|0\rangle$ denotes the ground state (all molecules in the ground state). The energy of the $k$th exciton is given by

$$\Omega_k = \omega_0 + 2J \cos\left(\frac{\pi k}{N+1}\right). \tag{3}$$

As is well known, the $k = 1$ state dominates the absorption spectrum of the ordered aggregate if all transition dipoles are parallel. If we discard homogeneous line broadening (see below), the related absorption line has zero width. At finite disorder, however, this changes. The static disorder has two effects: (i) It adds a random component to the frequency $\Omega_k$ of the $k$ states. (ii) It mixes the $k$ states with each other due to the fact that translational symmetry is broken by the disorder. As long as the mixing interaction is small compared to the spectral separation between the $k = 1$ and the $k = 2$ states, the $k = 1$ state still dominates the absorption spectrum and we may account for the disorder in a perturbative way. One then finds that the disorder-induced shift, $\langle k = 1|\sum_n \varepsilon_n \hat{b}_n^\dagger \hat{b}_n|k = 1\rangle$, of the $k = 1$ level for a particular disorder realization $\{\varepsilon_n\}$ is roughly given by the average of the $N$ random molecular offsets $\varepsilon_n$. Thus, the absorption line width is determined by the width of the distribution of this average offset, which is given by $\sigma/\sqrt{N}$ for Gaussian disorder. This is the well-known exchange narrowing argument, which was first made by Knapp [7]. If one considers the problem in somewhat more detail, one finds that the $k$ states of the linear chain are, in fact, shifted by a *weighted* average of the molecular offsets $\{\varepsilon_n\}$, which eventually gives for the absorption line width (HWHM) in the perturbative (i.e., small-disorder) regime [14,15]:

$$W = \sigma \sqrt{\frac{3}{2(N+1)}}. \tag{4}$$

In practice, aggregates are mostly too long or the disorder is too strong to neglect the mixing of the exciton states. The properly mixed exciton states are localized on part of the aggregate, with a typical length $N_{\mathrm{del}}$. Obviously, the width is then no longer determined by the aggregate size, but instead one thinks of the disordered aggregate as being built up from ordered segments of effective length $N_{\mathrm{del}}$. Using Eq. (4) this leads to a relation between the line width and the delocalization length:

$$W = \sigma \sqrt{\frac{3}{2(N_{\mathrm{del}}+1)}}. \tag{5}$$

It is known from numerical simulations that this heuristic exchange narrowing argument works rather well [13,16], so that it seems justified to use Eq. (5) to determine the delocalization length in a particular aggregate ensemble by measuring $W$. This method has indeed been used in the literature (see, e.g., Ref. [8]). A serious drawback of the method, however, is that one needs input on the value of $\sigma$. This is usually taken from the absorption line width of dilute solutions, in which aggregation plays no role. Obviously, however, the disorder strength felt by a single molecule in an aggregate may be quite different from the dilute-solution situation. As it is difficult to obtain direct experimental information on $\sigma$, the exchange narrowing method is very uncertain.

We now turn to the second method to relate the line width to the delocalization length. For increasing disorder, oscillator strength is transferred from the $k = 1$ state to the higher exciton states. For small disorder, only the mixing between the lowest states is important and the typical width over which the oscillator strength is distributed is then determined by the splitting between the two lowest exciton states:

$$\Delta E = \Omega_{k=2} - \Omega_{k=1} \approx \frac{3\pi^2|J|}{(N+1)^2}. \tag{6}$$

As long as the disorder is not too large, these exciton states are still visible as separate lines. When the disorder increases more and more, however, the excitons localize and the lines due to the various $k$ states merge into one broader line, whose typical width is given by $\Delta E$ as in Eq. (6) with $N$ replaced by $N_{\mathrm{del}}$

$$W = \frac{3\pi^2|J|}{(N_{\mathrm{del}}+1)^2}. \tag{7}$$

Eq. (7) suggests that the delocalization length may be obtained from the observed absorption line width $W$ (HWHM) through

$$N_{\mathrm{del}}^{W} = \sqrt{\frac{3\pi^2|J|}{W}} - 1, \tag{8}$$

where we use the superscript "$W$" to indicate the origin of this measure for the delocalization length. The advantage of this measure over the usual exchange narrowing argument, is that generally the position of the aggregate absorption band gives independent information about the interaction strength $J$, so that all quantities in the right-hand side of Eq. (8) are known with a reasonable accuracy.

In the next section, we will present results of a numerical check of the validity of this measure for the delocalization length. Before doing that, however, we note that indirect support for this measure is obtained from equating the expressions (5) and (7) for $W$. Doing so, one can eliminate $N_{\mathrm{del}}$, from which one finds $W \sim \sigma^{4/3}$. This powerlaw behavior in the intermediate disorder regime ($1 \ll N_{\mathrm{del}} \ll N$) has indeed been confirmed in many analytical and numerical studies (see, e.g., Refs. [12,13]). The derivation which we have given here for this scaling is very similar to the one presented by Malyshev [14].

## 3. Numerical results

We have studied the validity of the measure Eq. (8) for the delocalization length by performing numerical simulations. The absorption spectrum was simulated for linear aggregates of 250 molecules with parallel transition dipoles and with a disorder strength varying from $\sigma = 0.001|J|$ to $0.3|J|$. In these calculations, we also allowed for a finite homogeneous line width by giving each individual exciton transition a Lorentzian line shape of width $\gamma$ (HWHM). This is equivalent to convoluting the spectrum for $\gamma = 0$ with this Lorentzian. Details of these simulations can be found in Ref. [11]. For each $\sigma$, the width $W$ of the thus simulated absorption line was measured, from which we calculated $N_{\mathrm{del}}^{W}$ according to Eq. (8). At the same time, we calculated a reference delocalization length $N_{\mathrm{del}}$ directly from the simulated exciton wave functions through the participation ratio at the position $\omega_c$ of the maximum of the absorption spectrum. This well-known measure for single-particle localization reads [17,12,13]

$$\mathscr{P}(\omega) = \frac{\langle \sum_k \delta(\omega - \Omega_k) \rangle}{\langle \sum_k (\sum_n \varphi_{kn}^4) \delta(\omega - \Omega_k) \rangle}, \tag{9}$$

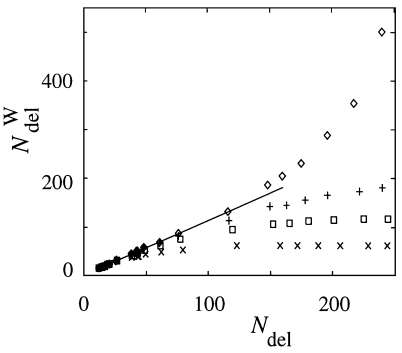


Fig. 1. Exciton delocalization length $N_{\mathrm{del}}^{W}$ obtained from the simulated linear absorption spectrum for $J$ aggregates of $N = 250$ molecules long, plotted against the delocalization length calculated from the participation ratio at the $J$ band center. Data points correspond to $\gamma/|J| = 0$ ($\diamond$), $8 \cdot 10^{-4}$ ($+$), $2 \cdot 10^{-3}$ ($\square$), and $8 \cdot 10^{-3}$ ($\times$), respectively. The solid line is the best linear fit through the 11 lowest data points for $\gamma = 0$, with slope $a = 1.12$ and abscissa $b = 1.86$.

where $\langle \cdots \rangle$ indicates the disorder average. Based on the fact that for the $k$ states in perfectly ordered chains, $\sum_n (\varphi_{kn})^4 = 3/(2(N+1))$, we define as reference ("real") value for the delocalization length

$$N_{\mathrm{del}} = \tfrac{3}{2}\mathscr{P}(\omega_c) - 1. \tag{10}$$

In Fig. 1, we present our results by plotting, for each disorder strength $\sigma$ considered, the value of $N_{\mathrm{del}}^{W}$ against the delocalization length obtained from the participation ratio. In this figure, one moves from right to left when increasing the disorder. We first focus on the data for vanishing homogeneous linewidth ($\diamond$), for which we see up to a delocalization length of about 120 (i.e., half the physical chain length) a well-defined linear scaling:

$$N_{\mathrm{del}}^{W} = aN_{\mathrm{del}} + b, \tag{11}$$

where the best fit is obtained for $a = 1.12$ and $b = 1.86$. The breakdown of the linear scaling at higher delocalization lengths is due to the fact that we then run out of the intermediate disorder regime, where Eq. (7) breaks down. In fact, if the disorder becomes so small that the excitons are almost completely delocalized, the spectrum is a series of well-separated $\delta$ peaks dominated by the peak due to the $k = 1$ exciton state. This explains why $N_{\mathrm{del}}^{W}$ diverges when $N_{\mathrm{del}} \to 250$.

We now turn to the inclusion of a finite homogeneous line width $\gamma$. Fig. 1 also shows $N_{\mathrm{del}}^{W}$ for three different choices of $\gamma$. It is observed that for small delocalization lengths, these data follow the same linear scaling as in the case $\gamma = 0$. If $N_{\mathrm{del}}$ increases, however, the linear scaling

breaks down and $N_{\rm del}^W$ underestimates the real delocalization length imposed by the static disorder. The reason is clear: the homogeneous broadening adds an extra contribution to $W$, which is not related to the static disorder. With decreasing disorder strength, i.e., with increasing delocalization length, the homogeneous component starts to dominate the total line width $W$, which then no longer gives information on the actual delocalization length. In fact, the maximum value for $N_{\rm del}^W$ that can be found in the presence of homogeneous broadening is given by $\sqrt{3\pi^2|J|/\gamma} - 1$. The linear scaling breaks down well before the delocalization length reaches this value. Of course, if one has independent information on the homogeneous linewidth, one may deconvolute the observed spectra into the homogeneous Lorentzian and the inhomogeneous lineshape imposed by static disorder. Using only the width of the latter component in the right-hand side of Eq. (8) will then give a good measure for the delocalization length, provided one is indeed in the intermediate-disorder regime. We stress that this simple approach relies on the assumption that the exciton homogeneous linewidth does not strongly depend on the exciton frequency, which generally is an oversimplification.

## 4. Applications

We first consider the example of PIC $J$ aggregates. This system has been studied extensively. We will focus on PIC aggregates in a low temperature (1.5 K) glassy host. The absorption line width under these conditions is $W = 13\ {\rm cm}^{-1}$ [18], while the homogeneous line width is negligibly small ($\gamma < 1\ {\rm cm}^{-1}$) [19]. Using as interaction strength $J = -600\ {\rm cm}^{-1}$, we arrive at $N_{\rm del}^W \approx 36$. This is to be compared to the value $N_{\rm del} \approx 50$ obtained from a full numerical simulation of the cooperative spontaneous emission and the line shape [13,18]. Considering the crudeness of our arguments, the comparison is rather good. This even improves if we realize that in the full numerical simulations long-range dipole–dipole interactions were taken into account. We may do this effectively by increasing the value of $J$ by 20% [13], which gives $N_{\rm del}^W \approx 40$. In addition, it should be realized that in Ref. [13] the delocalization length was taken at the frequency where the average oscillator strength per state is maximal and this happens on the blue side of the $J$ band, where the delocalization length is somewhat larger than at the top of the $J$ band. Finally, we note that using $W = 13\ {\rm cm}^{-1}$ and $N_{\rm del}^W = 40$ in Eq. (5), we find $\sigma = 68\ {\rm cm}^{-1}$, which agrees very well with the value $\sigma = 0.11|J| = 66\ {\rm cm}^{-1}$ obtained from the full numerical analysis in Refs. [13,18].

We next turn to the B850 ring in the bacterial light harvesting system LH2. The transfer interaction in this system is $J \approx -300\ {\rm cm}^{-1}$, while various values of the homogeneous and total linewidth (HWHM) have been reported. Here we quote two sets of data. Small and co-workers [20] report $W = 140\ {\rm cm}^{-1}$ and $\gamma = 105\ {\rm cm}^{-1}$ at 4.2 K. Thus, the homogeneous broadening is important. If we nevertheless neglect this broadening, we arrive at $N_{\rm del}^W \approx 7$. Correcting the total linewidth for homogeneous broadening by quadratic subtraction ($\sqrt{W^2 - \gamma^2}$), we arrive at $N_{\rm del}^W \approx 9$. Fleming and co-workers [5] report $W = 215\ {\rm cm}^{-1}$ and $\gamma = 94\ {\rm cm}^{-1}$ (room temperature), which in a similar way leads to $N_{\rm del}^W \approx 5.5$–6. We thus find a fairly large range for the delocalization length (5.5–9) obtained from the linear absorption spectrum. Our values touch on the upper boundary of the range around $N_{\rm del} \approx 4$, which has been quoted in several studies [2,3,5], while they are appreciably smaller than the delocalization over (almost) the full ring ($N_{\rm del} = 18$) which also has been claimed by various groups [1,4,6].

We stress that our numbers obtained for the LH2 complex should be considered with caution. First, our general simulations focussed on long aggregates with delocalization lengths larger than 10 molecules, while here we extrapolated our conclusions to small rings with delocalization lengths of at most 10 molecules. Actually, the circular structure may change the scaling factor $a$ by an amount in the order of 15% (due to $3\pi^2$ changing to $4\pi^2$). Second, we have assumed that the different disorder offsets $\varepsilon_n$ within one aggregate are completely uncorrelated. This may be too strong an assumption [7,15]. In a simple model that accounts for correlations within each aggregate, one distinguishes intra-aggregate disorder and inter-aggregate disorder. The intra-aggregate disorder is of the same type as we have considered above, i.e., for each molecule in a given aggregate, the disorder offsets are chosen independently from a Gaussian distribution with width $\sigma$. On the other hand, the inter-aggregate disorder adds to each molecular offset within a given aggregate exactly the same extra contribution, which for each aggregate is chosen randomly from a Gaussian with width $\sigma_{\rm inter}$. In this model, the observed absorption line width is determined by both $\sigma$ and $\sigma_{\rm inter}$. In fact, one expects this width to be of the order $(\sigma^2/N_{\rm del} + \sigma_{\rm inter}^2)^{1/2}$. On the other hand, the exciton delocalization length is not affected by the inter-aggregate disorder and is only determined by $\sigma$. Therefore, if the inter-aggregate disorder is appreciable (implying relatively large correlations between the offsets within each aggregate), the delocalization length obtained from the ensemble averaged absorption line width underestimates the actual delocalization length. Thus, the rather large absorption line width observed for the LH2 complex, may still be reconcilable with a delocalization over almost the entire ring, if the inter-complex disorder strength is comparable or larger than the exchange narrowed intra-complex disorder strength.

## 5. Conclusions

We conclude from our simulations that the observed width $W$ (HWHM) of the linear absorption spectrum is a useful measure for the exciton delocalization length imposed by uncorrelated static disorder. The value obtained from $W$ according to Eq. (8) slightly overestimates (by 10%) the delocalization length as obtained from the participation ratio at the center of the absorption band. This measure is superior to the value obtained from the commonly known exchange narrowing argument (Eq. (15)), as $J$ is usually known with reasonable accuracy, while $\sigma$ can only be guessed. Two conditions apply for the use of Eq. (8). First, we should be in the intermediate disorder regime, where $N_{\mathrm{del}}$ is at most of the order of half the physical aggregate length. Second, the homogeneous linewidth $\gamma$ should be negligible. If the latter does not hold, a rough measure for the delocalization length imposed by static disorder may still be obtained by using for $W$ in Eq. (8) the observed HWHM corrected for the necessary deconvolution to take the homogeneous component out of the absorption line. Alternatively, one may in the case of large homogeneous linewidth interprete $N_{\mathrm{del}}^{W}$ obtained from the complete linewidth (without correction) as the coherence size of the exciton imposed by scattering on both static disorder and dynamic degrees of freedom [4]. We have applied our method to PIC $J$ aggregates and the bacterial antenna complex LH2 (Section 4).

We finally note that a measure for the delocalization length that is closely related to $N_{\mathrm{del}}^{W}$ is provided by the pump–probe spectrum, which also is sensitive to the separation between the two lowest exciton states on a delocalization interval. Here, similar provisions concerning the effect of homogeneous broadening apply. For a detailed study of this delocalization measure, we refer to Ref. [11].

## References

[1] K. Sauer, R.J. Cogdell, S.M. Prince, A. Freer, N.W. Isaacs, H. Scheer, Photochem. Photobiol. 64 (1996) 564.
[2] R. Monshouwer, M. Abrahamsson, F. van Mourik, R. van Grondelle, J. Phys. Chem. B 101 (1997) 7241.
[3] M. Chachisvilis, O. Kühn, T. Pullerits, V. Sundström, J. Phys. Chem. B 101 (1997) 7275.
[4] T. Meier, V. Chernyak, S. Mukamel, J. Phys. Chem. B 101 (1997) 7332.
[5] R. Jimenez, F. van Mourik, G.R. Fleming, J. Phys. Chem. B 101 (1997) 7350.
[6] A.M. van Oijen, M. Ketelaars, J. Köhler, T.J. Aartsma, J. Schmidt, Science 285 (1999) 400.
[7] E.W. Knapp, Chem. Phys. 85 (1984) 73.
[8] S. de Boer, K.J. Vink, D.A. Wiersma, Chem. Phys. Lett. 137 (1987) 99.
[9] S. de Boer, D.A. Wiersma, Chem. Phys. Lett. 165 (1990) 45.
[10] G. Juzeliūnas, Z. Phys. D 8 (1988) 379.
[11] L.D. Bakalis, J. Knoester, J. Phys. Chem. B 103 (1999) 6620.
[12] M. Schreiber, Y. Toyozawa, J. Phys. Soc. Japan 51 (1982) 1528; ibid. 1537.
[13] H. Fidder, J. Knoester, D.A. Wiersma, J. Chem. Phys. 95 (1991) 7880.
[14] V. Malyshev, J. Lumin. 55 (1993) 225.
[15] J. Knoester, J. Chem. Phys. 99 (1993) 8466.
[16] V.A. Malyshev, P. Moreno, Phys. Rev. B 51 (1995) 14 587.
[17] D.J. Thouless, Phys. Rep. 13 (1974) 93.
[18] H. Fidder, D.A. Wiersma, Phys. Rev. Lett. 66 (1991) 1501.
[19] H. Fidder, J. Knoester, D.A. Wiersma, Chem. Phys. Lett. 171 (1990) 529.
[20] N.R.S. Reddy, R. Picorel, G.J. Small, J. Phys. Chem. B 96 (1992) 6458.